Partial oxidation of propane over rubidium-promoted MoO_3/SiO_2 catalyst

F. Solymosi and K. Kedves

Reaction Kinetics Research Group of the Hungarian Academy of Science and Institute of Solid State and Radiochemistry, University of Szeged, PO Box 168, H-6701 Szeged, Hungary

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Silica-supported Rb_2MoO_4 and rubidium-promoted MoO_3 were used as catalysts for the partial oxidation of propane in a fixed-bed continuous-flow reactor at 770–823 K using N_2O as oxidant. The main hydrocarbon products of the reaction were propylene, ethylene, propanal and methane. Addition of various compounds of rubidium to the MoO_3/SiO_2 greatly enhanced the conversion of propane and promoted the formation of propanal at the expense of ethylene and propylene. The highest yield for the production of this compound was found over Rb_2MoO_4/SiO_2 catalyst.

KEY WORDS: propane oxidation; propanal production; oxidative dehydrogenation; oxidation with dinitrogen oxide; silica-supported molybdenum oxide catalyst; alkali metal promoters; rubidium molybdate catalyst

1. Introduction

It has been observed before that the rate of the oxidation of hydrocarbons and its product distribution are sensitive to the nature of the oxidant [1,2]. In the case of the selective oxidation of ethane on silica-supported MoO_3 and V_2O_5 higher yields of partial oxidation products were achieved when N_2O was used instead of O_2 [3–8]. The performance of both V_2O_5 and MoO_3 catalysts was influenced by the nature of the support, and by the presence of a small amount of alkali metal salts [7–11]. Supported Mo oxides have been found to be very active catalysts in the oxidative dehydrogenation of propane using O_2 as an oxidant [2,12–16]. Taking into account the above mentioned features in the present work we examine the partial oxidation of propane on alkali-dosed MoO_3 deposited on silica.

2. Experimental

The oxidation of propane was carried out in a fixed-bed continuous-flow reactor. The reactor consisted of a quartz tube (7 mm i.d. × 130 mm) which was connected to a capillary tube (2 mm i.d.) so that the products could be rapidly removed from the heated zone. Generally, 0.3 g of sample was used as catalyst. The reacting gas mixture consisted of 12.5% of propane, 25.0% of N_2O, and Ar as diluent. The flow rate of the reactant was 40 ml/min. Analyses of the exit gases were performed with a Hewlett–Packard 5890 gas chromatograph. The temperature-programmed reduction (TPR) of the catalyst samples was carried out in the catalytic reactor. The catalysts were flushed with Ar containing 10% H_2 and the reactor was heated linearly up to 1000 K, while the H_2 consumption was determined. The catalysts were prepared by impregnation of a silica support (Cab-O-Sil) with a basic solution of ammonium paramolybdate or Rb_2MoO_4 to yield a nominal 2 wt% of MoO_3. When the catalyst was promoted with rubidium, a solution of a rubidium compound (Rb_2SO_4, $RbNO_3$ or Rb_2CO_3) was added to the solution of ammonium heptamolybdate before impregnation. The ratio of the Rb ion to the Mo ion was the same as in the case of Rb_2MoO_4. Rb_2MoO_4 was prepared by the method of Retgers [17]. After impregnation the catalysts were dried and calcined in air at 870 K for 5 h.

3. Results and discussion

For characterization of the catalysts, we determined the BET areas of the samples and their reducibility. Data obtained are listed in table 1. The BET surface area of Rb-containing MoO_3/SiO_2 is greatly decreased except that of the Rb_2CO_3-promoted sample. As no such change was observed for alkali-doped, but MoO_3-free SiO_2 [10], it seems likely that solid-phase reactions occurred in the samples, producing different polymolybdates or heteropolymolybdates [18–21]. The reducibility of the catalysts was examined by TPR method. The reduction of MoO_3/SiO_2 starts above 673 K and occurs in two stages. Adding rubidium

Table 1
Some characteristic data for Mo catalysts.

Catalyst	BET area (m^2/g)	T_R (K)
MoO_3/SiO_2	203	750, 1000
$(MoO_3 + Rb_2SO_4)/SiO_2$	78	720, 940
$(MoO_3 + Rb_2CO_3)/SiO_2$	136	790, 870
$(MoO_3 + RbNO_3)/SiO_2$	86	720, 960
Rb_2MoO_4/SiO_2	62	683, 920

T_R = peak temperature of the TPR.

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salts to the MoO_3 caused the lowering of the peak temperatures of the reduction. Two characteristic TPR curves are displayed in figure 1, and the peak temperatures of the reduction of different samples are collected in table 1.

The oxidation of propane on the MoO_3/SiO_2 catalyst occurred at a measurable rate at 823 K. Hydrogen, propylene, ethylene and methane were the main products. Smaller amounts of CO_2, CO, acetaldehyde, acroleine were identified. Minor amount of ethane was also detected. The selectivity of propylene was 50–40%, and that of ethylene 15–20%. Interestingly, propanal was also formed with a selectivity of 12–14%. The initial conversion of propane was about 4–4.5%, which slowly decreased with time on stream. A steady-state activity was attained only after several hours. At this stage, the conversion of propane was about 1.5–2.0%. Changes of some characteristic data with time on stream are plotted in figure 2(A).

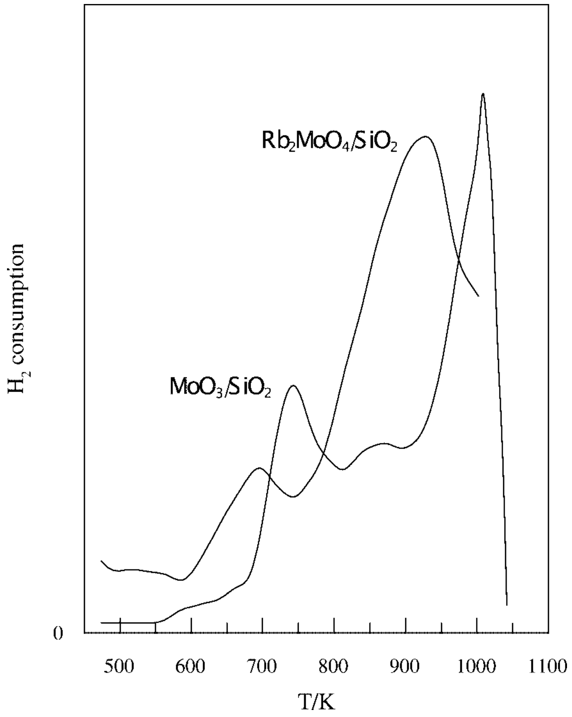

Figure 1. TPR curves of MoO_3/SiO_2 and Rb_2MoO_4.

The addition of the various rubidium compounds to MoO_3/SiO_2 enhanced the conversion of propane by a factor of 3–5. The marked increase in the activity cannot be attributed to a change in the surface area of the catalyst, as the addition of Rb salts to the MoO_3/SiO_2 catalyst significantly lowered the BET area of the sample (table 1). The rubidium additives markedly influenced the product distribution of the oxidation: the selectivity of propanal significantly increased, while that of propylene and ethylene formation decreased. A particular high activity was measured for Rb_2MoO_4 (figure 2(B)). The possible reason of this feature is that in this case the Mo catalyst and the Rb promoter may form a compound and thereby an intimate contact exists between them. The rates and the yields of various products for the different catalysts are collected in table 2.

Lowering the reaction temperature led to a significant increase in the selectivity to propanal and a decrease in that to ethylene. The selectivities to other compounds varied only slightly. This behavior is valid for all catalyst samples. In figure 3, we plotted the yield of the formation of main products for MoO_3/SiO_2 and Rb_2MoO_4/SiO_2. Note that the pure silica support exhibited very little activity towards propane oxidation (conversion of propane at 823 K was less than 0.5%) under similar conditions, and adding Rb_2CO_3 or $RbNO_3$ to silica caused no appreciable changes.

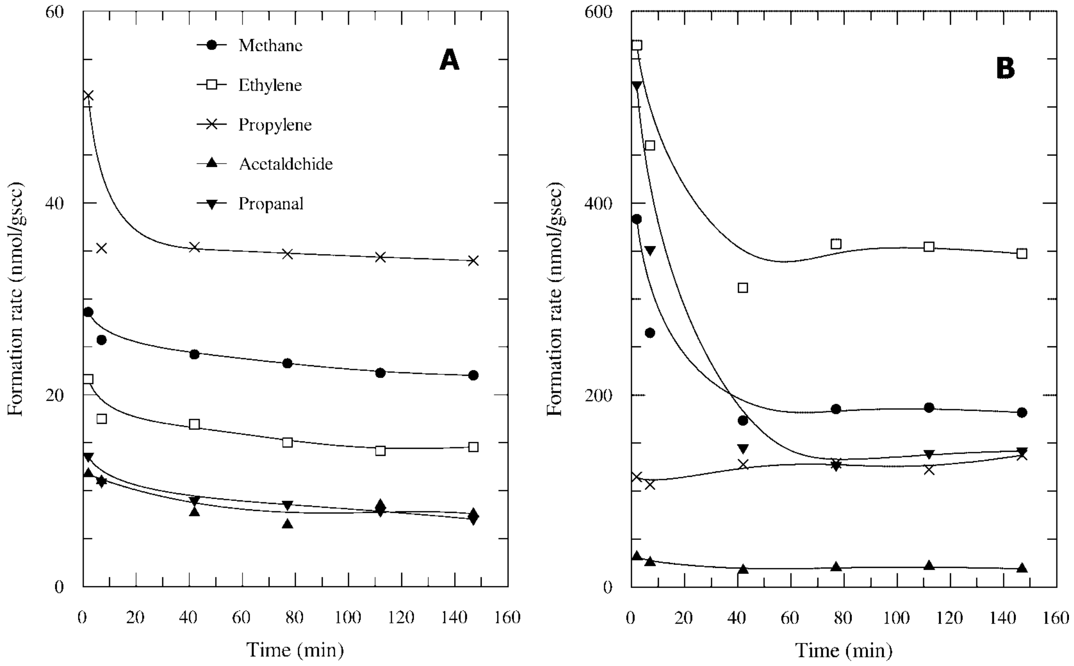

Figure 2. The rates of formation of various products in the oxidation of propane on MoO_3/SiO_2 (A) and Rb_2MoO_4/SiO_2 (B) at 823 K.

Variation of the contact time was examined on Rb_2MoO_4/SiO_2. We observed a relatively small influence on the product distribution. A decrease in this parameter by a factor of 3 by increasing the flow rate from 25 to 75 ml/min (the amount of catalyst was 0.3 g), decreased the conversion from 8.0 to 2.0% and the extent of total oxidation. At the same time it enhanced the selectivity of propylene from 13.5 to 21.0%, but influenced only slightly the selectivity of the formation of other hydrocarbons.

In conclusion, we can state that the addition of rubidium compounds to MoO_3 greatly increased the rate of propane oxidation; this is most probably connected with the enhanced formation and reactivity of Mo^{6+}–O^- sites which play an important role in the oxidation [5,22]. The species Mo^{6+}–O^- can be formed in the reaction of N_2O with reduced centers Mo^{5+}, the formation of which is facilitated in the presence of alkali metal salts. We may also take into account the occurrence of solid-state reactions between MoO_3 and SiO_2, producing various oxometalate species, such as polymolybdates, paramolybdates, molybdosilicic acid, *etc.* [18–21]; the molybdosilicic acid exhibited high activity in the oxidation of methane [19]. These compounds may be stabilized by rubidium salts.

As regards the product distribution, the Rb_2MoO_4 catalyst exhibited striking behavior, which differed from that of the other Rb-doped and undoped MoO_3 samples, as it promoted mainly the formation of propanal. This means that on Rb_2MoO_4 the reaction

$$\begin{aligned} &2Mo^{6+} + C_3H_7\text{–}O^- + OH^- \\ &\quad \rightleftharpoons C_2H_5CHO + H_2O + 2Mo^{5+} \end{aligned}$$

is favored (very probably due to smaller numbers of acidic sites) as compared to the reaction

$$C_3H_7\text{–}O^- \rightleftharpoons C_3H_6 + OH^-$$

which yields propylene and requires acidic sites [15].

Table 2

Effects of alkali compounds on the rates and yields of the formation of various products in the oxidation of propane with N_2O at 823 K.[a]

Catalyst	Rate[b] (nmol/g s)				Yield[b]			
	C_2H_4	C_3H_6	C_3H_6O	CH_4	C_2H_4	C_3H_6	C_3H_6O	CH_4
MoO_3	16.9	35.2	8.9	14.2	0.14	0.36	0.11	0.1
$MoO_3 + Rb_2CO_3$	94.2	72.7	235.7	44.5	0.7	0.81	2.63	0.17
$MoO_3 + Rb_2CO_3$	92.4	53.1	251.1	43.6	0.86	0.71	3.49	0.2
$MoO_3 + RbNO_3$	138.7	71.3	98.0	79.8	0.97	0.75	1.03	0.28
$MoO_3 + Rb_2SO_4$	100	65.5	94.5	44.1	0.8	0.79	1.14	0.18
Rb_2MoO_4	357.3	129.1	126.8	185.2	5.08	2.75	2.71	1.31
Rb_2MoO_4	268.6	121	160.5	101.1	3.51	2.37	3.15	0.66

[a] In all cases SiO_2 was used as a support.

[b] Steady-state values measured at 77 min of reaction.

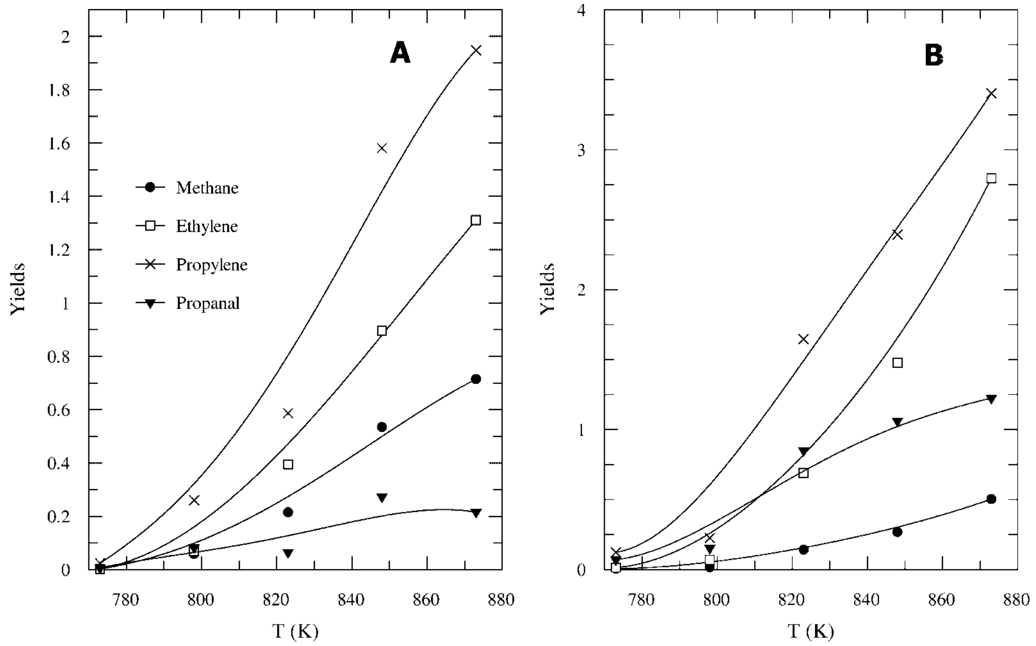

Figure 3. The effects of temperature on the yields of products formed in the oxidation of propane over (A) MoO_3/SiO_2 and (B) Rb_2MoO_4/SiO_2. Data are measured at steady state.

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